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(19) (CA) **CANADIAN PATENT** (12)

(54) 1,2,4-TRIAZOL-1-YL COMPOUNDS, THEIR  
MANUFACTURE, AND USE THEREOF AS FUNGICIDES

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ABSTRACT OF THE DISCLOSURE:

The present invention relates to new 1,2,4-triazol-1-yl compounds of the formula (I):



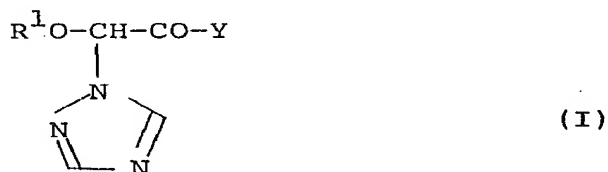
where  $\text{R}^1$  denotes phenyl substituted by cyclohexyl, phenyl, 1 to 3 halogen atoms or alkyl of 1 to 4 carbon atoms, and Y denotes  $\text{OR}^2$  or  $\text{N} \begin{array}{l} \nearrow \text{R}^3 \\ \searrow \text{R}^4 \end{array}$   $\text{R}^2$  denoting alkynyl of 3 to 15 carbon atoms,  $\text{R}^3$  denoting hydrogen, alkyl of 1 to 20 carbon atoms, alkenyl of 3 to 15 carbon atoms, phenyl or cyanoethyl, and  $\text{R}^4$  denoting phenyl, benzyl or phenyl or benzyl substituted by 1 or 2 halogen atoms, trifluoromethyl or alkyl of 1 to 4 carbon atoms, or alkenyl or alkynyl of 3 to 15 carbon carbon atoms, phenylethyl, naphthyl or cyanoethyl, and their plant-compatible salts and metal complexes. The above compounds have a good fungicidal action. This invention is also directed to the fungicides containing these compounds as active ingredients, and processes for combating fungi with these compounds.

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The present invention relates to new 1,2,4-triazole derivatives, processes for the manufacture thereof, and their use as fungicides.

It has been disclosed that t-butyl 2-(1',2',4'-triazol-1'-yl)-2-phenylacetate has a fungicidal action (German Laid-Open Application DE-OS 2,638,470). However, its action, particularly on mildews and rusts, is unsatisfactory. It is therefore hardly suitable for use as a crop protection agent for combating injurious fungi.

10 We have now found new compounds having a superior herbicidal action. The object of the invention was to provide new 1,2,4-triazol-1-yl compounds of the formula



where

20  $\text{R}^1$  denotes phenyl substituted by cyclohexyl, phenyl, 1 to 3 halogen atoms or alkyl of 1 to 4 carbon atoms, and

Y denotes  $\text{OR}^2$  or  $\text{N} \begin{array}{l} \diagup \text{R}^3 \\ \diagdown \text{R}^4 \end{array}$

$\text{R}^2$  denoting alkynyl of 3 to 15 carbon atoms,

$\text{R}^3$  denoting hydrogen, alkyl of 1 to 20 carbon atoms,

alkenyl of 3 to 15 carbon atoms, phenyl or cyanoethyl, and

30  $\text{R}^4$  denoting phenyl, benzyl or phenyl or benzyl substituted by 1 or 2 halogen atoms, trifluoromethyl or alkyl of 1 to 4 carbon atoms, or alkenyl or alkynyl of 3 to 15 carbon carbon atoms, phenylethyl, naphthyl or cyanoethyl, and their plant-compatible salts and metal complexes.

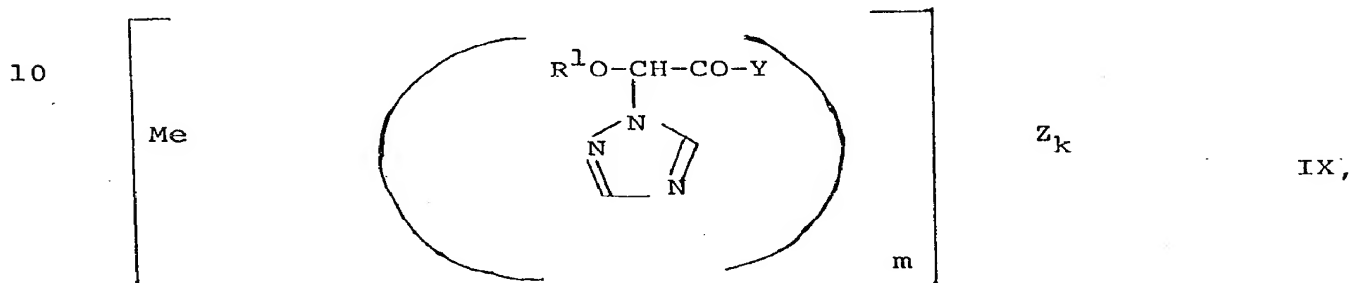
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In formule I,  $R^2$  preferably denotes 1-chlorobutyn-2-yl-4, 3-chlorobutyn-1-yl-4, 1-chloropentyn-2-yl-4, butyn-2-yl-1, butyn-1-yl-3, butyn-1-yl-4, 3-methylbutyn-1-yl-3 and 1-ethynylcyclohexyl.

Exemples of salts tolerated by crop plants are hydrochlorides, hydrobromides, sulfates, nitrates, phosphates, oxalates and dodecylbenzene sulfonates.

Metal complexes are compounds of the formula

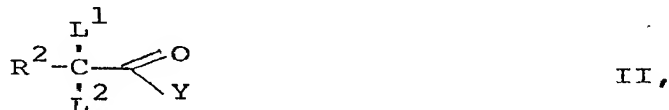


where  $R^1$  and Y have the above meanings, Me denotes a metal cation, e.g., of copper, zinc, tin, manganese, iron, cobalt or nickel, Z denotes the anion of an inorganic acid, e.g., hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, or hydrobromic acid, and k and m denote one of the integers 1, 2, 3 and 4.

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A further object of the invention is to provide a process for the manufacture of 1,2,4-triazolyl compounds of the formula I wherein

a) a compound of the formula



where  $R^2$  and Y have the above meanings and  $L^1$  and  $L^2$  are identical or different and are nucleophilically displaceable leaving groups, is reacted with a compound of the formula

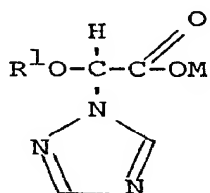
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where  $R^1$  has the above meanings, or a salt thereof, and with 1,2,4-triazole, or a salt thereof, in the presence or absence of a solvent or diluent and/or of an inorganic or organic base and in the presence or absence of a reaction accelerator at from  $0^\circ$  to  $180^\circ\text{C}$ , or

b) a compound of the formula



IV,

where  $R^1$  has the above meaning and M denotes hydrogen, one equivalent of a metal cation or a substituted or unsubstituted ammonium ion, is reacted with a compound of the formula

HY

V,

where Y has the above meanings, after or with simultaneous addition of reagents suitable for derivatizing acids, in the presence or absence of a solvent or diluent and/or of an inorganic or organic base and in the presence or absence of a reaction accelerator at from  $-20^\circ$  to  $+180^\circ\text{C}$ , or

c) a compound of the formula V is reacted with a compound of the formula

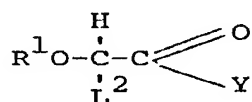
$L^3Y$

VI,

where Y has the above meanings and  $L^3$  is a nucleophilically displaceable leaving group, in the presence or absence of a solvent or diluent and/or an acid binder and in the presence or absence of a reaction accelerator at from  $-20^\circ$  to  $+180^\circ\text{C}$ , or

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d) a compound of the formula



VII,

where  $\text{R}^1$ , Y and  $\text{L}^2$  have the above meanings, is reacted with 1,2,4-triazole in the presence or absence of a solvent or diluent and/or an inorganic or organic base and in the presence or absence of a reaction accelerator at from  $-20^\circ$  to  $+180^\circ\text{C}$  and, if desired, the compounds obtained according to a) to d) are converted into salts and metal complexes tolerated by plants.

Examples of nucleophilically displaceable leaving groups  $\text{L}^1$  and  $\text{L}^2$  mentioned in processes a) and d) are halogen, such as chlorine, bromine and iodine; bisulfate; hydrogen sulfonate; and unsubstituted or substituted alkylsulfonyloxy, arylsulfonyloxy, alkylsulfate, phenoxy, phenylthio, oxonium, sulfonium or ammonium radicals. Suitable inorganic or organic bases which may if desired also be used as acid binders in reaction a) are, for example, alkali metal and alkaline earth metal hydroxides, such as sodium hydroxide, potassium hydroxide and calcium hydroxide; alkali metal carbonates, such as potassium and sodium carbonate; alkali metal hydrides, such as sodium hydride; alkali metal and alkaline earth metal alcoholates, such as sodium methylate, magnesium ethylate and sodium isopropylate; tertiary amines, such as trimethylamine, triethylamine, N,N-dimethylaniline, N,N-dimethylcyclohexylamine, N-methylpiperidine and pyridine; and azoles, such as 1,2,4-triazole and imidazole. However, other bases usually employed may also be used.

Examples of suitable salts of compounds of the formulae III and salts of 1,2,4-triazol are their alkali metal,

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alkaline earth metal, and substituted or unsubstituted ammonium salts.

The preferred solvents or diluents include halo-hydrocarbons, such as methylene chloride, chloroform, 1,2-dichloroethane and chlorobenzene; aliphatic or aromatic hydrocarbons, such as cyclohexane, petroleum ether, benzene, toluene and xylenes; alcohols, such as methanol, ethanol, isopropanol and n-butanol; esters, such as ethyl acetate; amides, such as dimethylformamide; nitriles, such as acetronitrile; sulfoxides, such as dimethylsulfoxide; ketones, such as acetone and methyl ethyl ketone; ethers, such as diethyl ether, tetrahydrofuran and dioxane, and mixtures of the above. Advantageously, the solvent or diluent is used in an amount of from 100 to 2,000 wt%, preferably from 100 to 1,000 wt%, based on starting materials II or III.

Preferred reaction accelerators are metal halides such as sodium bromide and potassium iodide, crown ethers, quaternary ammonium compounds, such as tetrabutylammonium iodide, acids, or combinations of these compounds.

The process according to the invention is in general carried out at from 40° to 150°C, for from 1 to 60 hours, under atmospheric or superatmospheric pressure, and continuously or batchwise.

In carrying out the process according to the invention, the amounts employed per mole of compound II are in general from 0.5 to 2 moles of compound III and 1,2,4-triazole, preferably from 0.9 to 1.3 moles of III and 1,2,4-triazole, from 1 to 4 moles, preferably from 1.8 to 2.3 moles, of base, and, if a reaction accelerator is used, from 0.01 to 0.1 mole thereof.

In a preferred form of process a) according to the invention, the starting materials III and 1,2,4-triazole are

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mixed, in optional sequence, with a base and a diluent, the starting material II, with or without a reaction accelerator, is then added and the reaction is carried out at from 40° to 150°C, for from 0.5 to 120, preferably from 1 to 60, hours.

To isolate the compounds according to the invention, the diluent is, if desired, removed, and the residue is taken up in a suitable solvent and washed with water to remove excess base and unreacted starting materials of the formula III and 1,2,4-triazole. In general, the products remaining after  
10 removal of the solvent do not require any further purification, but if necessary they can be additionally purified by conventional methods, such as recrystallization, extraction and chromatography.

The following are - without restricting the invention to them - examples of conventional reagents suitable for derivatizing acids for process b): proton or Lewis acids, inorganic and organic acid halides, such as thionyl chloride, phosphorus pentachloride and acetyl chloride; chlorocarbonic acid esters, such as the ethyl, tert-butyl and benzyl esters;  
20 anhydrides, such as ketene; diimides, such as N,N'-dicyclohexylcarbodiimide; and carbonyl or sulfonyl diazoles, such as carbonyldiimidazole, carbonylditriazole, sulfonyldiimidazole and sulfonylditriazole.

For process c), particularly suitable compounds of the formula VI are those in which L<sup>3</sup> is a nucleophilically displaceable leaving group, such as halogen, e.g., chlorine, bromine and iodine; substituted or unsubstituted alkyl- or arylsulfonyloxy, such as mesyloxy, trifluoromethylsulfonyloxy, brosyloxy and tosyloxy; an alkyl sulfate, such as methyl  
30 sulfate; and the diazo group.

Preferred solvents or diluents and acid binders preferably used for processes b), c) and d) are those given

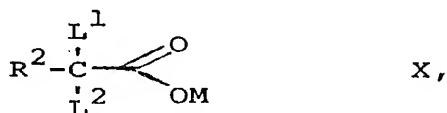


for process a).

The reactions according to processes b), c) and d) described in general terms and the isolation of the compounds according to the invention are carried out in conventional manner (cf. Houben-Weyl, 8, 508 et seq., and 653 et seq., Stuttgart, 1952, and 15, 2, Stuttgart, 1974).

The starting materials of the formula IV may be produced by reaction of a compound of the formula

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where  $\text{R}^2$ ,  $\text{L}^1$ ,  $\text{L}^2$  and M have the above meanings, with a hydroxy compound of the formula



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where  $\text{R}^1$  has the above meanings, or a salt thereof, and with 1,2,4-triazole or a salt thereof, in the presence or absence of a diluent and/or an acid binder and in the presence or absence of a reaction accelerator, at from 0° to 180°C.

The starting materials of the formula VII may be prepared by conventional methods, e.g., by halogenation of the corresponding aryl- or heteroaryloxyalkanoic acid derivatives (c.f. German Laid-Open Application DE-OS 1,808,034).

The compounds of the formula I have one or more chiral centers; pure isomers can be obtained from the mixtures, obtained by synthesis, in accordance with prior art methods.

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The pure isomers and also mixtures thereof may be used.

The following examples illustrate the production of the new compounds.

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### Manufacture of the starting materials

a) 90 parts of a technical-grade sodium methylate solution in methanol (30 parts of sodium methylate in 100 parts of solution) is added to 81.5 parts of 2,4-dichlorophenol and 34.5 parts of 1,2,4-triazole in 300 parts of ethanol and after brief stirring 109 parts of dibromoacetic acid is introduced. The mixture is refluxed for 14 hours, the solvent is stripped off and the residue is dissolved in about 1,000 parts of water. While cooling, the pH is brought to 1 by adding concentrated hydrochloric acid, and the precipitate which has formed is filtered off and washed with isopropanol. After drying, 121 parts of 2-(2',4'-dichlorophenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid, of melting point 211-213°C (with decomposition), is obtained.

b) 771 parts of 4-chlorophenol and 414 parts of 1,2,4-triazole are added to 1,080 parts of a technical-grade sodium methylate solution in methanol (30 parts of sodium methylate in 100 parts of solution). After briefly stirring the mixture, 774 parts of dichloroacetic acid is run in, during which addition the temperature rises to about 60°C. The methanol is then distilled off and isopropanol is run in at the same time in such amount that the reaction mixture can be stirred without difficulty. When the internal temperature has reached 80°C, boiling is continued for 10 hours, the solvent is then distilled off, ice water is added and the mixture is acidified with concentrated hydrochloric acid. The precipitate formed is filtered off, washed with isopropanol and dried. 676 parts (58% of theory) of 2-(4'-chlorophenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid of melting point 205-207°C (with decomposition) is obtained.

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### Manufacture of the end products

#### EXAMPLE 1

25 parts of 2-(4'-chlorophenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid was introduced into 100 parts of methylene chloride, and 0.5 part of dimethylformamide and 15 parts of triethylamine were added. The reaction mixture was cooled to -10°C, and 15 parts of thionyl chloride was dripped in while stirring. The mixture was then stirred overnight at room temperature. A solution of 12 parts of triethylamine and 12 parts of aniline in 20 parts of methylene chloride was dripped in at +10°C with cooling. The mixture was then refluxed for 1 hour. After the mixture had cooled, the precipitate was filtered off and washed with methylene chloride, and the organic phase was concentrated. The oil which remained was filtered through silica gel using methylene chloride as eluant, and 18 parts of a uniform oil was obtained which crystallized after standing overnight in ether.

The yield was 15 parts of 2-(4'-chlorophenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid anilide of melting point 134° to 136°C.

#### EXAMPLE 2

23 parts of 2-(4'-phenylphenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid was suspended in 150 parts of tetrahydrofuran; 13 parts of N,N'-carbonyldiimidazole was added in portions to this suspension. After the mixture had been stirred for 1 hour at room temperature, a solution of 9 parts of 4-fluoroaniline in 20 parts of tetrahydrofuran was dripped in. The mixture was stirred for 12 hours and then stirred into 1,000 parts of ice water, and the precipitate was filtered and dried.


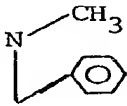

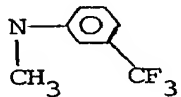
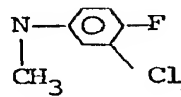
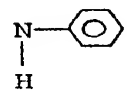

There was obtained 26 parts of 2-(4'-phenylphenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid-p-fluoroanilide of melting point 92° to 96°C.

Table

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	X	Y	Fp/n <sub>D</sub> <sup>20</sup>
3	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	OC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	91-94
4	2,4-DiBr-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	OC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	
5	2-Br-4-Cl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	OC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	
6	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	OC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	60-63
7	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NHC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	112-115
8	2,4-DiCH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NHC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	
9	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NHC(CH <sub>3</sub> ) <sub>2</sub> C≡CH	74-82
10	3-F-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NHC(CH <sub>3</sub> ) <sub>2</sub> CH≡CH <sub>2</sub>	
11	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NHC <sub>6</sub> H <sub>5</sub>	92-95
12	2,4-DiCH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub>	H	H	H	O	NHC <sub>6</sub> H <sub>5</sub>	114-116
13	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-2-F-C <sub>6</sub> H <sub>4</sub>	99-101
14	4-Br-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-2-F-C <sub>6</sub> H <sub>4</sub>	
15	4-Cl-C <sub>6</sub> H <sub>4</sub>	H	H	H	O	NH-3-F-C <sub>6</sub> H <sub>4</sub>	102-105
16	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3-F-C <sub>6</sub> H <sub>4</sub>	80-84
17	3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-3-F-C <sub>6</sub> H <sub>4</sub>	
18	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-4-C <sub>6</sub> H <sub>4</sub>	138-142
19	2,4,5-TriCl-C <sub>6</sub> H <sub>2</sub> -H		H	H	O	NH-4-F-C <sub>6</sub> H <sub>4</sub>	136-140
20	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-4-F-C <sub>6</sub> H <sub>4</sub>	139-142
21	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-4-Cl-C <sub>6</sub> H <sub>4</sub>	146-149
22	2-Br-4-Cl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-4-Cl-C <sub>6</sub> H <sub>4</sub>	
23	3-F-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-4-Cl-C <sub>6</sub> H <sub>4</sub>	
24	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-2,4-DiF-C <sub>6</sub> H <sub>3</sub>	122-124
25	3,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3,4-DiF-C <sub>6</sub> H <sub>3</sub>	
26	2,4-DiCH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3Cl-4F-C <sub>6</sub> H <sub>3</sub>	
27	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3,5-DiCl-C <sub>6</sub> H <sub>3</sub>	170-173
28	3-CHF <sub>2</sub> -CF <sub>2</sub> O-C <sub>6</sub> H <sub>4</sub> -H		H	H	O	NH-3,5-DiCl-C <sub>6</sub> H <sub>3</sub>	
29	4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	H	H	O	NH-2-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	
30	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-2-i-C <sub>3</sub> H <sub>7</sub> -C <sub>6</sub> H <sub>4</sub>	90-94
31	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-3-tert-C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	153-158

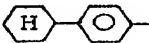
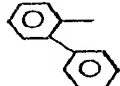
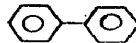


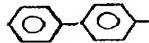
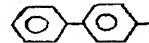
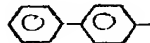
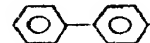
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Table

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	X	Y	Fp/n <sub>D</sub> <sup>20</sup>
32	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3-tert-C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub>	154-155
33	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	121-124
34	4-tert-C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-3-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	
35	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-3CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	115-122
36	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	oil
37	3-F-C <sub>6</sub> H <sub>4</sub> -	H	H	H	S	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	
10 38	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N(CH <sub>3</sub> )-4-Cl-C <sub>6</sub> H <sub>4</sub>	125-127
39	2,4-DiCl-C <sub>3</sub> H <sub>3</sub> -	H	H	H	O	NH-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	72-75
40	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N(CH <sub>3</sub> )CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1,5652
41	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH- 	144-146
42	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	N- 	106-108
43	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH- 	152-156
20 44	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N- 	1,526
45	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N- 	1,530
46	4-F-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N- 	102-110
47	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	145-148
30 48	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	N-CH <sub>2</sub> -CH=CH <sub>2</sub> 	76-77
49	3,5-DiCH <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	101-103
50	4-tert-C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-4F-C <sub>6</sub> H <sub>4</sub>	123-125

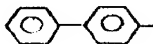
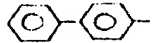
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Table

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	X	Y	Fp/n <sub>D</sub> <sup>20</sup>
51	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	N-2,4-DiCl-C <sub>6</sub> H <sub>3</sub>   CH <sub>3</sub>	109-111
52	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N(CH <sub>2</sub> CH <sub>2</sub> CN) <sub>2</sub>	1,529
53		H	H	H	O	NH-C <sub>6</sub> H <sub>5</sub>	120-123
54	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N-C <sub>6</sub> H <sub>5</sub>   CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	74-76
55	4-Cl-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	N(CH <sub>2</sub> -CH=CH <sub>2</sub> ) <sub>2</sub>	1,5280
56		H	H	H	O	NH-C <sub>6</sub> H <sub>5</sub>	110-113
57	2,4,5-TriCl-C <sub>6</sub> H <sub>2</sub> -	H	H	H	O	NHC(CH <sub>3</sub> ) <sub>2</sub> C=CH	176-185
58	4-F-C <sub>6</sub> H <sub>4</sub> -	H	H	H	O	NH-4F-C <sub>6</sub> H <sub>4</sub>	127-135
59		H	H	H	O	NH- 	105-111
60	2,4,5-TriCl-C <sub>6</sub> H <sub>2</sub>	H	H	H	O	NHCH <sub>2</sub> - 	168-172
61		H	H	H	O	NH-C <sub>6</sub> H <sub>5</sub>	158-163
62		H	H	H	O	N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub>	69-74
63	2,4-DiCl-C <sub>6</sub> H <sub>3</sub>	H	H	H	O	NH-CH-C <sub>6</sub> H <sub>5</sub>   CH <sub>3</sub>	102-103
64	2,4-DiCl-C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NH-CH <sub>2</sub> -2Cl-C <sub>6</sub> H <sub>4</sub>	102-105
65	3-tert-C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> -	H	H	H	O	NHC <sub>6</sub> H <sub>5</sub>	103-106
66		H	H	H	O	NH-4Cl-C <sub>6</sub> H <sub>4</sub>	120-125
67		H	H	H	O	NHCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	71-76

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Table

No.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	X	Y	Fp/n <sub>D</sub> <sup>20</sup>
68		H	H	H	O	N(CH <sub>2</sub> -CH=CH <sub>2</sub> ) <sub>2</sub>	49-54
69		H	H	H	O	NH-3CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	120-125

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The manufacture of the metal complexes is illustrated by the following non limitative example.

### EXAMPLE 70

17 parts of 2-(4'-phenylphenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid-4-fluoroanilide was dissolved in 200 parts of ethanol at 35°C; a solution of 14 parts of copper (II) chloride in 100 parts of ethanol was then added. The mixture was stirred for 2 hours and cooled to 15°C, and the precipitate filtered.

10           There was obtained 13 parts of bis- $\sqrt{2}$ -(4'-phenylphenoxy)-2-(1',2',4'-triazol-1'-yl)-acetic acid-4-fluoroanilide $\sqrt{7}$ -copper (II) chloride of melting point 176° to 180°C.

The other compounds can be converted into their metal complexes in analogous manner.

The compounds according to the invention and their salts and metal complexes have an excellent action on a broad spectrum of fungi, especially plant-pathogenic fungi, particularly from the Ascomycetes and Basidiomycetes classes. Some of them have a systemic action and may be used as foliar and  
20   soil fungicides.

The fungicides according to the invention are of particular interest for combatting numerous fungi in various crop plants or their seed.

By "crop plants", we mean in the connection in particular wheat, rye, barley, oats, rice, Indian corn, cotton soybeans, coffee, sugarcane, fruit and ornamentals in horticulture, and vegetables such as cucumbers, beans and Cucurbitaceae.

The new compounds are especially suitable for  
30   combatting the following diseases: Erysiphe graminis in cereals, Erysiphe cichoriacearum in Cucurbitaceae, Posdosphaera leucotricha in apples, Uncinula necator in grapes, Erysiphe polygoni in beans, Sphaerotheca pannosa in roses, Puccinia species in cereals, Rhizoctonia solani in cotton,



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Helminthosporium species in cereals, Ustilago species in cereals and sugarcane, Rhynchosporium secalis in cereals, and Venturia inaequalis (apple scab).

The compounds are applied by spraying or dusting the plants with the active ingredients or treating their seed with them. They may be applied before or after infection of the plants or seed by the fungi.

The compounds of the invention can be converted into the conventional formulations, e.g. solutions, emulsions, 10 suspensions, dusts, powders, pastes and granules. The form of application depends entirely on the purpose for which the agents are being used; it should, however, ensure a fine and uniform distribution of the active ingredient. The formulations are prepared in the conventional manner, for example by diluting the active ingredient with solvent and/or carriers, with or without the addition of emulsifiers and dispersants and, where water is used as the diluent, with or without organic auxiliary solvents. Suitable auxiliaries are, essentially, solvents for example aromatics, e.g., xylene and benzene, 20 chloroaromatics, e.g. chlorobenzene, paraffins, e.g. petroleum fractions, alcohols, e.g. methanol and butanol, amines, e.g., ethanolamine, dimethylformamide, and water; solid carriers, for example natural rock powders, e.g. kaolin, alumina, talc and chalk, and synthetic rock powders, e.g. highly disperse silica and silicates; emulsifiers, for example non-ionic and anionic emulsifiers, e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates, and dispersants, for example lignin, sulfite waste liquors and methylcellulose.

The agents in general contain from 0.1 to 95% 30 by weight of active ingredient, preferably from 0.5 to 90%.

The application rates depend on the type of effect desired, and are from 0.01 to 3, but preferably from 0.01 to

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1, kg of active ingredient per hectare.

The agents, and the ready-to-use preparations obtained therefrom, e.g., solutions, emulsions, suspensions, powders, dust, pastes or granules, are applied in conventional manner, e.g. by spraying, atomizing, dusting, broadcasting, dressing seed, or watering.

Examples of such formulations are as follows.

- I. 90 parts by weight of the compound of Example 6 is mixed with 10 parts by weight of N-methyl- $\alpha$ -pyrrolidone. A mixture is obtained which is suitable for application in the form of very fine drops.
- II. 20 parts by weight of the compound of Example 32 is dissolved in a mixture consisting of 80 parts by weight of xylene, 10 parts by weight of the adduct of 8 to 10 moles of ethylene oxide with 1 mole of oleic acid-N-monoethanolamide, 5 parts by weight of the calcium salts of dodecylbenzenesulfonic acid, and 5 parts by weight of the adduct of 40 moles of ethylene oxide with 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.
- III. 20 parts by weight of the compound of Example 17 is dissolved in a mixture consisting of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 moles of ethylene oxide with 1 mole of isooctylphenol, and 10 parts by weight of the adduct of 40 moles of ethylene oxide to 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and finely distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.
- IV. 20 parts by weight of compound of Example 56 is dissolved in a mixture consisting of 25 parts by weight of

cyclohexanol, 65 parts by weight of a mineral oil fraction having a boiling point between 210° and 280°C, and 10 parts by weight of the adduct of 40 moles of ethylene oxide with 1 mole of castor oil. By pouring the solution into 100,000 parts by weight of water and uniformly distributing it therein, an aqueous dispersion is obtained containing 0.02% by weight of the active ingredient.

V. 20 parts by weight of the compound of Example 58 is well mixed with 3 parts by weight of the sodium salt of diisobutyl naphthalene- $\alpha$ -sulfonic acid, 17 parts by weight of the sodium salt of a lignin-sulfonic acid obtained from a sulfite waste liquor, and 60 parts by weight of powdered silica gel, and triturated in a hammer mill. By uniformly distributing the mixture in 20,000 parts by weight of water, a spray liquor is obtained containing 0.1% by weight of the active ingredient.

VI. 3 parts by weight of the compound of Example 30 is intimately mixed with 97 parts by weight of particulate kaolin. A dust is obtained containing 3% by weight of the active ingredient.

VII. 30 parts by weight of the compound of Example 2 is intimately mixed with a mixture consisting of 92 parts by weight of powdered silica gel and 8 parts by weight of paraffin oil which has been sprayed onto the surface of this silica gel. A formulation of the active ingredient is obtained having good adherence.

VIII. 40 parts by weight of the compound of Example 1 is intimately mixed with 10 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate, 2 parts of silica gel and 48 parts of water to give a stable aqueous dispersion. Dilution in 100,000 parts by weight of water gives an aqueous dispersion containing 0.04 wt% of active

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ingredient.

IX. 20 parts of the compound of Example 2 is intimately mixed with 2 parts of the calcium salt of dodecylbenzenesulfonic acid, 8 parts of a fatty alcohol polyglycol ether, 2 parts of the sodium salt of a phenolsulfonic acid-urea-formaldehyde condensate and 68 parts of a paraffinic mineral oil. A stable oily dispersion is obtained.

The above ready-to-use preparations may contain other active ingredients together with those according to the invention, e.g., herbicides, insecticides, growth regulators and other fungicides or may be mixed with fertilizers and applied together with these. When the active ingredients are mixed with other fungicides, the fungicidal spectrum of action is in many cases broadened.

The list of fungicides given below, with which the compounds according to the invention can be combined, is intended to illustrate the possible combinations, but the invention is in no way limited to these.

Examples of fungicides which may be combined with the compounds according to the invention are as follows.

Dithiocarbamates and derivatives thereof, such as  
ferric dimethyldithiocarbamate  
zinc dimethyldithiocarbamate  
manganese ethylenebisdithiocarbamate  
zinc ethylenebisdithiocarbamate  
tetramethylthiuram disulfide  
manganese-zinc ethylenediamine-bisdithiocarbamate  
zinc-(N,N'-propylene-bisdithiocarbamate)  
ammonia complex of zinc-(N,N'-ethylene)-bisdithiocarbamate  
and  
N,N'-polyethylene-bis-(thiocarbamoyl)-disulfide  
ammonia complex of zinc-(N,N'-propylene-bisdithiocarbamate)

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and

N,N'-polypropylene-bis-(thiocarbamoyl)-disulfide

nitro derivatives, such as

dinitro-(1-methylheptyl)-phenylcrotonate

2-sec-butyl-4,6-dinitrophenyl-3,5-dimethylacrylate

2-sec-butyl-4,6-dinitrophenylisopropylcarbonate

heterocyclic structures, such as

N-trichloromethylthiotetrahydrophthalimide

N-trichloromethylthiophthalimide

10. 2-heptadecyl-2-imidazoline acetate

2,4-dichloro-6-(o-chloroanilino)-s-triazine

0,0-diethylphthalimidophosphorothionate

5-amino-1-[bis-(dimethylamino)-phosphinyl]-3-phenyl-1,2,4-triazole

5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole

2,3-dicyano-1,4-dithiaanthraquinone

2-thio-1,3-dithio-(4,5b)-quinoxaline

methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate

2-methoxycarbonylamino benzimidazole

20. 2-thiocyanomethylthiobenzothiazole

4-(2-chlorophenylhydrazono)-3-methyl-5-isooxazolone

pyridine-2-thiol-1-oxide

8-hydroxyquinoline and its copper salt

2,3-dihydro-5-carboxanilido-6-methyl-1,4,-oxathin-4,4-dioxide

2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiin

2-[furyl-(2)]-benzimidazole

piperazine-1,4-diyl-bis[1-(2,2,2-trichloroethyl)-formamide]

2-[thiazolyl-(4)]-benzimidazole

5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine

30. bis-(p-chlorophenyl)-3-pyridinemethanol

1,2-bis-(3-ethoxycarbonyl-2-thioureido)-benzene

1,2-bis-(3-methoxycarbonyl)-2-thioureido)-benzene

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and various fungicides, such as

dodecylguanidine acetate

3-[2-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]-glutarimide

hexachlorobenzene

N-dichlorofluoromethylthio-N,N'-dimethyl-N-phenylsulfuric acid  
diamide

2,5-dimethyl-furan-3-carboxylic acid anilide

2,5-dimethyl-furan-3-carboxylic acid cyclohexylamide

2-methyl-benzoic acid anilide

10 2-iodo-benzoic acid anilide

1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane

2,6-dimethyl-N-tridecyl-morpholine and its salts

2,6-dimethyl-N-cyclododecyl-morpholine and its salts

DL-methyl-N-(2,6-dimethylphenyl)-N-furoyl-(2)-alaninate

DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl-alanine methyl  
ester

diisopropyl 5-nitroisophthalate

1-(1',2',4'-triazolyl-1')-[1-(4'-chlorophenoxy)]-3,3-dimethyl-  
butan-2-one

20 1-(1',2',4'-triazolyl-1')-[1-(4'-chlorophenoxy)]-3,3-dimethyl-  
butane-2-ol

N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-aminobutyrolactone  
and

N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolylurea.

The following examples demonstrate the biological  
action of the new compounds. The agent used for comparison  
purposes was t-butyl 2-phenyl-2-(1',2',4'-triazol-1'-yl)-  
acetate (N) disclosed in German Laid-Open Application  
DE-OS 2,638,470.

30 EXAMPLE A

Leaves of pot-grown wheat seedlings of the "Caribo"  
variety are sprayed with aqueous emulsions consisting of 80%

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(by weight) of active ingredient and 20% of emulsifier, and dusted, 2 days after the sprayed-on layer has dried, with spores of wheat mildew (Erysiphe graminis var. tritici). The plants are then placed in a greenhouse at 18° to 24°C. The extent of mildew spread is determined after 10 days.

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Compound from Example No.	Leaf attack after spraying with liquor containing active ingredient in amounts of		
	0.025%	0.012%	0.006%
1	0	0	0
2	0	0	0
3	0	2	3
11	0	0	2
12	1	1	2
13	0	0	0
14	0	1	2
10 30	0	0	2-3
33	0	0	1
35	0	2	2-3
38	0	0	2
39	0	0	0
41	0	0	2
42	0	1	2
43	0	0	0
44	0	0	3
45	0	0	0
20 46	0	0	0
48	0	0	0
52	1	1	1
53	0	0	0
54	0	0	0
55	0	0	0
56	0	0	2
58	0	0	0
59	0	0	0
60	0	0	0
30 61	0	0	0
62	0	0	0
63	0	0	0



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Compound from Example No.	Leaf attack after spraying with liquor containing active ingredient in amounts of		
	0.025	0.012%	0.006%
64	0	0	0
65	0	2	2
66	0	0	2
67	0	0	0
68	0	0	0
69	0	0	1
70	0	0	0
10 N	2	3	4
Control (untreated)	5		

0 = no fungus growth, graduated down to 5 = leaf surface  
totally covered with fungus

## EXAMPLE B

Leaves of wheat plants grown in pots are artificially infected with spores of Puccinia recondita, and placed for 48 hours in a steam-saturated chamber at 20° to 25°C. The plants are then sprayed with aqueous liquor containing, as a solution or emulsion in the water, a mixture of 80% of the compound to be investigated and 20% of sodium ligninsulfonate. The plants are then set up in the greenhouse at from 20° to 22°C and a relative humidity of 75 to 80%. The extent of fungus spread is assessed after 10 days.

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Compound from Example No.	Leaf attack after spraying with liquor con- taining active ingredient in amounts of		
	0.025%	0.012%	0.006%

2	0	0	0
59	0	0	1
61	0	0	0
62	0	0	1
66	0	0	0
68	0	0	1
70	0	0	1

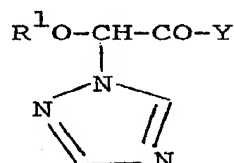
10

Control (untreated)	5
---------------------	---

0 = no fungus growth, graduated down to 5 = leaf surface totally covered with fungus.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A 1,2,4-Triazol-1-yl compound of the formula



I,

where

$\text{R}^1$  denotes phenyl substituted by cyclohexyl, phenyl, 1 to 3 halogen atoms or alkyl of 1 to 4 carbon atoms, and  
 $\text{Y}$  denotes  $\text{OR}^2$  or  $\text{N} \begin{array}{l} \nearrow \text{R}^3 \\ \searrow \text{R}^4 \end{array}$   
 $\text{R}^2$  denoting alkynyl of 3 to 15 carbon atoms,  
 $\text{R}^3$  denoting hydrogen, alkyl of 1 to 20 carbon atoms, alkenyl of 3 to 15 carbon atoms, phenyl or cyanoethyl, and  
 $\text{R}^4$  denoting phenyl, benzyl or phenyl or benzyl substituted by 1 or 2 halogen atoms, trifluoromethyl or alkyl of 1 to 4 carbon atoms, or alkenyl or alkynyl of 3 to 15 carbon atoms, phenylethyl, naphthyl or cyanoethyl, and their plant-compatible salts and metal complexes.

2. A compound selected from the group consisting of 2-(1',2',4'-triazol-1'-yl)-2-(4'-chlorophenoxy)-acetic acid anilide, 2-(1',2',4'-triazol-1'-yl)-2-(4'-phenylphenoxy)-acetic acid-p-fluoroanilide, and 2-(1',2',4'-triazol-1'-yl)-2-(4'-chlorophenoxy)-acetic acid- $\alpha$ -naphthylamide.

3. A process for manufacturing a compound as claimed in claim 1, wherein

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a) a compound of the formula

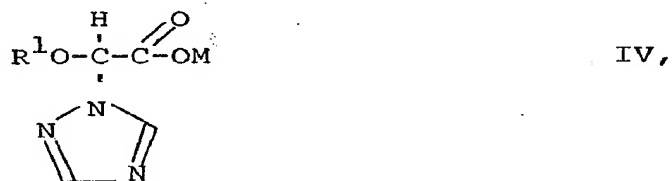


where  $\text{R}^2$  and  $\text{Y}$  have the above meanings and  $\text{L}^1$  and  $\text{L}^2$  are identical or different and are nucleophilically displaceable leaving groups, is reacted with a compound of the formula



where  $\text{R}^1$  has the above meanings, or a salt thereof, and with 1,2,4-triazole, or a salt thereof, in the presence or absence of a solvent or diluent and/or of an inorganic or organic base and in the presence or absence of a reaction accelerator at from  $0^\circ$  to  $180^\circ\text{C}$ , or

b) a compound of the formula



where  $\text{R}^1$  has the above meaning and  $\text{M}$  denotes hydrogen, one equivalent of a metal cation or a substituted or unsubstituted ammonium ion, is reacted with a compound of the formula



where  $\text{Y}$  has the above meanings, after or with simultaneous addition of reagents suitable for derivatizing acids, in the presence or absence of a solvent or diluent and/or of an

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inorganic or organic base and in the presence or absence of a reaction accelerator at from  $-20^{\circ}$  to  $+180^{\circ}\text{C}$ , or

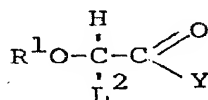
c) a compound of the formula V is reacted with a compound of the formula



VI,

where Y has the above meanings and  $\text{L}^3$  is a nucleophilically displaceable leaving group, in the presence or absence of a solvent or diluent and/or an acid binder and in the presence or absence of a reaction accelerator at from  $-20^{\circ}$  to  $+180^{\circ}\text{C}$ , or

d) a compound of the formula



VII,

where  $\text{R}^1$ , Y and  $\text{L}^2$  have the above meanings, is reacted with 1,2,4-triazole in the presence or absence of a solvent or diluent and/or an inorganic or organic base and in the presence or absence of a reaction accelerator at from  $-20^{\circ}$  to  $+180^{\circ}\text{C}$  and, if desired, the compounds obtained according to a) to d) are converted into salts and metal complexes tolerated by plants.



**SUBSTITUTE**  
***REMPLACEMENT***

**SECTION is not Present**  
***Cette Section est Absente***